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ANTIMICROBIAL ACRYLIC FIBER

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15. SUBJECT TERMS
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ANTIMICROBIAL ACRYLIC FIBER

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ABSTRACT

Fibers have been produced from a blend of poly(acrylonitrile) and poly(styrene hydantoin). The fibers were extruded from a single solvent, dimethyl acetamide. The fibers could be chlorinated to produce halamines and thus rendered antimicrobial. The ability to regenerate the halamines (and the antimicrobial functionality) lasted through 50 home laundry washings. The chlorine absorption was shown to be proportional to the specific surface area of the fibers, as might be expected for hydrophobic materials which can react in water only on the fiber surface.

***Keywords*:** antimicrobial fiber, antimicrobial polymer, biocidal modified polyacrylonitrile

1. Introduction

Inactivation of microorganisms, which cause odor as well as contagious diseases, is a desirable goal of biocides. Numerous antimicrobial materials have been developed over to the years as mankind has moved toward this goal [1]. While it is desirable that biocidal materials should be strong inactivating agents for microorganisms, they should not be harmful to other life or the environment.

Fibers and fabrics are among the materials that are closely associated with humans, and for which antimicrobial functionality would be useful. One can easily recognize the benefit of biocidal hospital clothing and furnishings, as well as upholstery, carpets and bedding for the general public.

Work on *N*-halamines as biocidal agents has been ongoing for over two decades [13,15]. This work builds on the well known ability of *N*-halamine compounds such as 1,3-dihalo-5,5-dimethylhydantoin and halogenated isocyanurates to hold and stabilize chlorine in areas such as swimming pools [10]. Initially, our work produced water soluble imides, amides, and amines which were used (in halamine form) as dispersed antimicrobials for water treatment [14]. Subsequently, the nitrogen functionality was immobilized in a polymer, poly(styrenehydantoin), or PSH [7]. Over the last few years, we have attached the halamine precursors onto a variety of materials including textile fibers [3], wall surfaces [11], glass [2], sand [5], etc. This has necessitated the attachment of a variety of reactive groups to the halamine precursor, depending on the material to which it would be attached. The attaching groups, which have proved useful, include methylol/formaldehyde [4] and siloxane [11,12]. Much work concerning *N*-halamine biocidal textiles has also been done elsewhere [6,8,9]. Some work has also been done on simply mixing of halamine precursors with materials, for example during extrusion, to produce stable matrix structures, without the necessity of a covalent binding functionality. Since chemical bonding is the strongest connecting force between molecules, it should be the best way for application of antimicrobial compounds to fibers; however, as certain biocidal polymers have no appropriate functional groups for chemical bonding, blending with fiber-forming polymeric

materials to make antimicrobial fibers could result in a useful alternative. This paper reports on one of these mixtures.

Poly(acrylonitrile) (PAN) is one of the standard fiber-forming materials, and it has been used as a wool substitute because it is easily made into a bulky yarn. As low molecular weight, uncrosslinked PSH and PAN are both soluble in dimethylacetamide (DMAc, normally used for the extrusion of PAN), the solution might provide a route to fibers containing both polymers. An acrylic fiber containing PSH (Figure 1) might be expected to allow formation of chloramines on the surface and therefore be useful as an antimicrobial fiber.

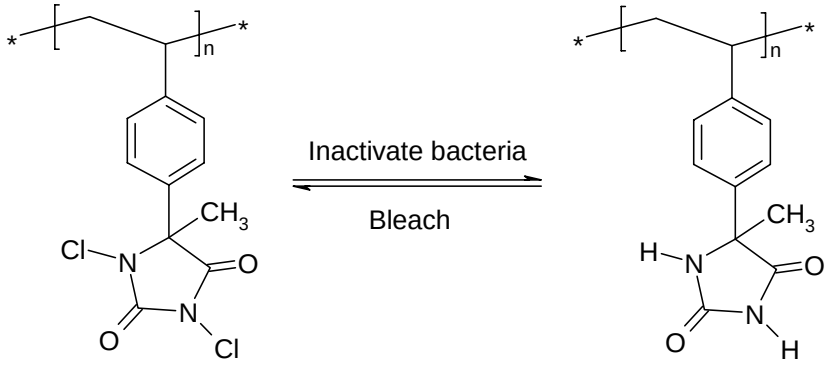

Figure 1 The function of disinfection of polystyrene hydantoin

2. Experimental

2.1. Materials

PSH used was synthesized by an established procedure [7] in a molecular weight range of 800 - 5000. The PAN was a fiber forming acrylonitrile copolymer; it was obtained from Solutia Inc. (St. Louis, MO). Dimethylacetamide was purchased from Fisher (Fair Lawn, NJ). All solvents, unless otherwise stated, were of reagent grade, and used without further purification.

2.2. Preparation of PAN/PSH Solution

Appropriate amounts of PSH were dissolved in 70 mL of DMAc, after which 7 g of PAN were added to the DMAc/PSH to produce a solution of approximately 10% PAN. The ratios of PAN/PSH were varied from 100/0 to 100/12 (by weight). The blended solution was stirred for 24 h at 70ºC. The solution was allowed to store for more than 2 h at 70ºC without stirring to remove air bubbles, after which it was poured into a piston wet spinning apparatus.

2.3. Wet Spinning Process

The piston pump (ISCO, Series D piston pump) was fitted with a single hole (1.25 mm diameter circular) spinneret. The set-up consisted of extruder, a coagulating bath (using tap water), a stepped godet with four levels and a take-up winder. The blended solutions in the extruder cylinder were maintained 35ºC, and forced through the spinneret fitted with a 325 mesh wire screen filter inside. Extrusion conditions were as follows:

Process:	dry-jet wet spinning
Extrusion temperature:	35ºC
Throughput:	0.16~0.64 mL/min
Coagulation bath:	tap water
Godet speed:	12.5~50 RPM
Drawing:	3 stage, steps 1, 2, 3, and 4
Draw ratio:	3.9
Take-up speed:	2.0 - 8.1 m/min

After wet spinning, the yarns were soaked in tap water at ambient temperature for 24 h to extract the solvent, which was used for spinning.

2.4. Measurement of Physical Properties

Tensile properties were investigated with a universal materials testing machine (Instron Model 1122) at 22ºC and 65% humidity. The data were obtained by averages of 10 tests. The length between upper and lower jaw was 25.4 mm, and the crosshead speed was 20 mm/min.

2.5. Chlorination and Titration

A commercial 6% sodium hypochlorite solution was used to chlorinate the fabrics (diluted to 3300 ppm of the commercial strength with distilled water) at pH 8 to produce biocidal materials. After soaking the fabric in the solution at ambient temperature for 30 min, and rinsing with a large excess of distilled water, the samples were dried at 45ºC for 2 h to remove any unbonded chlorine.
An iodometric/thiosulfate titration procedure was used to analyze oxidative chlorine content. The $[Cl^+]$% in the sample was calculated with the following equation:

$$[Cl^+]\% = (V \times N \times 35.45) / (W \times 2 \times 10)$$

Where $[Cl^+]$% is the wt % of oxidative chlorine on the sample, V is equal to the volume of the titrant (sodium thiosulfate solution, mL), N is equal to the normality of the titrant, and W is the weight of the sample (g).

2.6. Laundering Test

The American Association of Textile Chemists and Colorists (AATCC) Test Method 61-2001 was used to investigate the stability of PSH and chlorine in/on the fibers after home laundering. A Launder-Ometer fitted with stainless steel cylinders (3 x 5 in) including 150 mL of 0.2% AATCC detergent solution and 50 stainless steel balls was rotated for 45 min at 42± 0.5 RPM and 49ºC. These conditions are estimated to be equivalent to 5 washing cycles in a home laundry. After detaching the cylinders, the fibers inside each cylinder were rinsed with three 300 mL portions of distilled water and air dried at ambient temperature.

2.7. Antimicrobial Test

After making the fibers into a crude nonwoven fabric (one inch square), treated samples were challenged with *Staphylococcus aureus* (ATCC 6538) using a modified AATCC Test Method 100-1999. After applying bacteria suspensions in pH7 phosphate buffer solution to the samples,

and covering with another swatch. After contact times of 30 min, the samples were quenched with 5.0 mL of sterile 0.02 N sodium thiosulfate solution. Serial dilutions of the quenched samples were made using pH 7 phosphate buffer and plated on Trypticase soy agar. The plates were incubated at 37ºC for 24 h and then counted to determine the presence or absence of viable bacteria.

3. Results and Discussion

3.1. Properties and Chlorine Content of the Fibers

FT-IR was employed to prove the existence of PSH in the composite fiber and prominent features in Figure 2 show that the carbonyl bands of PSH appeared at 1728 cm^{-1} and 1772 cm^{-1} (Figure 2, c). The PAN/PSH composite fiber exhibits the same carbonyl bands (Figure 2, b) with a third band at 2245 cm^{-1} corresponding to the PAN C≡N present. This is compelling evidence that the composite fiber contains both PSH and PAN.

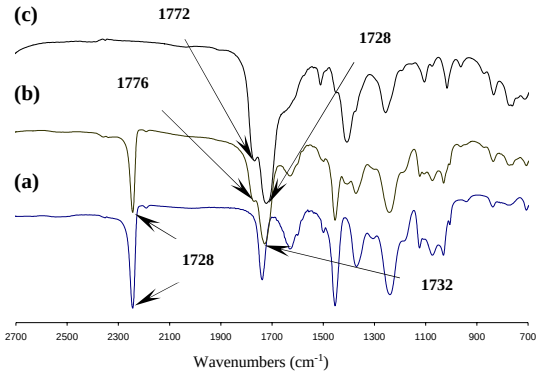

Figure 2 FT-IR bands of the composite fibers of (a) PAN/PSH (100/0), (b) PAN/PSH (100/12), and (c) PSH powder

The tensile properties of samples were measured at 65% humidity and 22ºC after conditioning the samples for 24 h. The results in Table 1 indicate that increasing the PSH content of the fiber increases the chlorine content after chlorination; however, as the PSH content increased, tenacity was decreased. It is presumed that the presence of the PSH may lower packing density of PAN resulting in a decreased tenacity. Due to PSH has a phenyl group as well as a hydantoin ring on the repeating unit, the bulky side chain could promote the disorder of PAN chains. Extrusion conditions were not, however, optimized for fiber properties.

Table 1 Mechanical properties and chlorine content of the acrylics
(0.2 mL/min of extrusion velocity and 50 RPM of a take-up speed)

Ratio[a] (PAN/PSH)	*100/0*	*100/4*	*100/8*	*100/12*
$[Cl^+]$ %	0	0.01	0.05	0.07
Denier (g/9000m)	21.2 ±4.1	20.1 ±2.7	27.9 ±5.8	29.2 ±5.3
Tenacity (g/den)	1.50 ±0.16	1.33 ±0.11	0.99 ±0.05	0.92 ±0.16
Strain at break	55.3 ±15.8	54.5 ±10.6	12.3 ±16.5	15.6 ±11.5

(%)	

[a] PAN/PSH by weight

As denier decreased, the blended acrylic released (absorbed) more chlorine. The results are indicated in Table 2.

Table 2 Variation of chlorine content of PAN/PSH(100/12) fibers with various deniers (Take-up speed: 12.5 RPM)

Extrusion velocity (mL/min)	*Denier (g/9000 m)*	*Surface area (m^2/g)*	*$[Cl^+]$ %*	*Atoms/cm^2*
0.64	398	1.57×10^{-2}	0.02	2.16×10^{16}
0.32	179	2.34×10^{-2}	0.04	2.90×10^{16}
0.16	85	3.39×10^{-2}	0.07	3.51×10^{16}
0.16 [a]	21 [b]	6.86×10^{-2}	0.11	2.72×10^{16}
N/A	1	31.10×10^{-2}	0.50[b]	2.21×10^{16}

[a] Take-up speed: 50RPM.
[b] Predicted value.

It is suggested that poly(acrylonitrile) has limited moisture absorption due to inherent hydrophobicity, and as a result, only PSH on the surface of the fiber is active in absorbing chlorine and inactivating bacteria. Due to that the theoretical $[Cl^+]$% of PSH is 24.87. If all of the added PSH is chlorinated, theoretical $[Cl^+]$% of PAN/PSH (100/12) should be 2.66. For the 21 denier fiber (21 g/900 m), the chlorine content was only 0.11% indicating that we have chlorinated 4.1% of the available PSH sites. Since thinner fibers have more surface area, one would expect that thinner fibers would have greater chlorine retention and antibacterial activity at lower PSH content. The effect of surface area on absorbed chlorine is shown in Figure 3. Using the graph in Figure 3, and extrapolating to a surface area corresponding to a denier of 1, we would expect a Cl^+ content of 0.50% which corresponds to 18.80% of theoretical chlorine absorption.

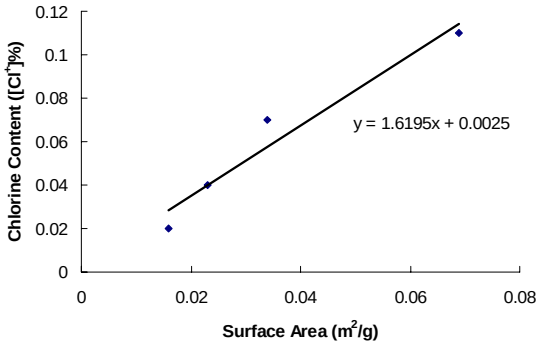

Figure 3 Variation of chlorine content of PAN/PSH (100/12) fibers with various surface areas

3.2. Durability, Rechargeability, and Antimicrobial Efficacies

The relative durability of chlorine to laundering and rechargeability afterwards (with Cl) was evaluated; the results appear in Table 3.

Table 3 Durability and rechargeability of the acrylics (0.16 mL/min of extrusion velocity and 50 RPM of a take-up speed)

unit: $[Cl^+]$%

Ratio [a] *(PAN/PSH)*	*100/0*	*100/4*	*100/8*	*100/12*
Chlorinated sample	0	0.03	0.07	0.11
Washing 50 cycles	0	0.01	0.01	0.05
Recharge after washing 50 cycles	0	0.04	0.07	0.10

[a] PAN/PSH by weight

All of blended acrylics retained little of their antimicrobial properties after 50 washes; however, after recharging, the fibers with household bleach, they regained almost all of their original chlorine content. During the washing test, the hydrophobic properties of the PAN, which is a major component, prohibited the swelling of the fibers. For this reason, the migration of the PSH out of PAN could be limited, and increased durability appeared. Even the surface of the fibers obtained chlorine after chlorination.

The fibers were formed into a nonwoven matt which upon chlorination with 10% household bleach became antimicrobial. The results are shown in Table 4. From the data, most of chlorinated acrylic nonwovens caused complete inactivation of *S. aureus* in 30 min.

table 4 Antimicrobial efficacy of PAN/PSH blended fiber against *Staphylococcus aureus*

Samples [a]		*Contact time (min)*	*Bacterial reduction*	
			(%)	Log Reduction
Unchlorinated fibers	PAN/PSH (100/0)	30	49	0.2
	PAN/PSH (100/4)	30	32	0.1
	PAN/PSH (100/8)	30	88	0.9
	PAN/PSH (100/12)	30	99.5	2.2
Chlorinated fibers	PAN/PSH (100/0)	30	94	1.2
	PAN/PSH (100/4)	30	99.9	3.3
	PAN/PSH (100/8)	30	100	6.5
	PAN/PSH (100/12)	30	100	6.5

[a] Each sample was inoculated with 25 µl of bacterial suspension at 3×10^6 cfu/ml. 6 log reduction corresponds to a 99.9999% kill of the bacteria.

4. Conclusions

An antimicrobial-fiber precursor (PAN/PSH composite fiber) was produced by dry-jet wet spinning. Strength properties and antibacterial effectiveness of the fiber were investigated. Strength properties were somewhat decreased as more PSH was added during extrusion; however, little effort has been made to optimize extrusion conditions.

As the PSH content increased, the absorbed chlorine and antibacterial effectiveness also increased. Since poly(acrylonitrile) is hydrophobic (has limited moisture absorption), it might be presumed that just PSH on the surface of the fibers is active in absorbing chlorine and inactivating bacteria. The fact that only a fraction of the theoretical chlorine absorption was observed, and the fact that absorbed chlorine is shown to increase with increasing surface area of the fiber, supports this theory. The treatment appears stable to repeated laundering, and the chlorinated acrylic fibers inactivated *Staphylococcus aureus* (Gram-positive bacteria) within 30 min.

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